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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵: C07C 381/00, C07D 213/71	A1	(11) International Publication Number: WO 94/22817 (43) International Publication Date: 13 October 1994 (13.10.94)
(21) International Application Number: PCT/GB94/00740 (22) International Filing Date: 7 April 1994 (07.04.94) (30) Priority Data: 9307245.2 7 April 1993 (07.04.93) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): WILLIAMS, Alfred, Glyn [GB/GB]; 1 Pitts Park, Binfield, Berkshire RG12 5ES (GB). FOSTER, Nicholas, Russell [GB/GB]; 46 Northcott, Hanworth, Bracknell, Berkshire RG12 7WR (GB). (74) Agents: RICKS, Michael, James et al.; ICI Group Patents Services Dept., Shire Park, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FL, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, TJ, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE PREPARATION OF ARYL- AND HETEROARYLSULPHURPENTAFLUORIDES (57) Abstract A process for the preparation of arylsulphurpentafluorides and heteroarylsulphurpentafluorides comprises reacting an aryldisulphide or heteroaryldisulphide with silver difluoride under anhydrous conditions at a temperature of at least 100 °C and in the presence of a non-aqueous solvent whose boiling point is at or above the reaction temperature, said solvent being substantially stable under the reaction conditions.		

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PROCESS FOR THE PREPARATION OF ARYL- AND HETEROARYLSULPHURPENTAFLUORIDES

The present invention relates to a process for the manufacture of aryl sulphurpentafluoride compounds and in particular to a process for the manufacture of benzenesulphurpentafluoride compounds and pyridine-sulphurpentafluoride compounds.

Aryl and heteroaryl sulphurpentafluoride compounds are useful in the manufacture of agrochemicals, as described for example in International Application No GB92/01636. Such compounds have however proved extremely difficult to prepare in a reasonable yield or in a commercially viable manner.

A method of preparing phenyl sulphurpentafluoride compounds such as meta and para nitrobenzenesulphurpentafluoride is described in J. Am. Chem. Soc. (84), 1964 page 3064 (William A Sheppard). The paper describes the reaction of phenyl disulphides or phenyl trisulphides with silver difluoride in a "Freon" solvent under reflux at 50-60°C followed by heating at 120°C. More specifically, meta and para nitrobenzenesulphurpentafluoride were prepared by reacting bis-(meta-nitrophenyl)-disulphide or bis-(para-nitrophenyl)-disulphide respectively with silver difluoride in the presence of $\text{CCl}_2\text{FCClF}_2$ at reflux for one hour. The $\text{CCl}_2\text{FCClF}_2$ was then distilled and the reaction mixture heated to 120°-135°C for 2 hours. After cooling, the reaction mixture was extracted with carbon tetrachloride and chloroform and the combined extracts were distilled to give the desired product. The yield in the case of meta nitrobenzenesulphurpentafluoride was 28-30% and in the case of para nitrobenzenesulphurpentafluoride was at best 16%.

We have now found that use of a suitable solvent in an improved process provides a commercially attractive method for the preparation of aryl and heteroaryl sulphurpentafluoride compounds.

According to the present invention there is provided a process for the preparation of arylsulphurpentafluorides and heteroarylsulphurpentafluorides which comprises reacting an aryl disulphide or heteroaryl disulphide with silver difluoride under anhydrous conditions at a temperature of at least 100°C and in the presence of a non-aqueous solvent whose boiling point is at or above the reaction temperature, said solvent being substantially stable under the reaction conditions.

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Whilst the present invention is not to be taken as being limited by any one particular theory, it is believed that the reaction scheme is as set out in Scheme 1, as illustrated for the preparation of a benzenesulphurpentafluoride compound wherein R_n represents n suitable substituents R such as are discussed below. It will be appreciated that the heteroatom in a heteroaryldisulphide starting material corresponding to (I) may be in any desired position in the ring. There is no need to isolate the aryl- or heteroarylsulphurtrifluoride intermediate such as (II) and indeed the intermediate is generally unstable.

The reaction preferably takes place at a temperature of at least 110°C. Temperatures in excess of 160°C may be used if desired but are likely to give rise to a reduced yield through the formation of by-products and may lead to a reduction in solvent stability, especially if a hydrocarbon solvent is used. Temperatures in the range 110-150°C, for example 120-140°C are especially preferred.

The solvent is selected to have a boiling point at or preferably above the reaction temperature. Thus preferred solvents have a boiling point of at least 120°C or more preferably at least 130°C, the reaction temperature being selected accordingly. The solvent should be substantially stable under the reaction conditions. By the term "substantially stable" is meant that the solvent is either substantially inert under the reaction conditions or that the solvent undergoes a fluorination reaction to yield a minor proportion (for example less than 5%) of a fluorinated derivative of the solvent which is itself a suitable solvent for the reaction. Solvents which undergo substantial reaction with silver difluoride or with the aryl- or heteroarylsulphurtrifluoride intermediate are not suitable. For this reason solvents having carbonyl, hydroxy, carboxylate or nitrile moieties are unlikely to be suitable.

It is not essential that the solvent should dissolve all reactants and final products, provided that it acts as an effective reaction medium. Indeed, the solubility of the silver difluoride is likely to be small in the reaction solvent.

Hydrocarbon solvents having an appropriate boiling point, for example octane, nonane or higher hydrocarbon solvents, are suitable for the process of the present invention. Such solvents may undergo some fluorination during the course of the reaction but, as discussed above, the resultant

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minor proportion of fluorinated solvent will in generally be equally effective as a solvent and such solvents are therefore considered "stable" as that term is used herein. In a continuous process in which the solvent is re-cycled, as discussed below, there may be a build-up fluorinated hydrocarbon solvent and an appropriate bleed may be necessary to maintain an appropriate proportion of non-fluorinated hydrocarbon solvent. Hydrocarbon solvents have the advantage of cheapness.

Chlorofluorohydrocarbon solvents and perfluorohydrocarbon solvents are generally more expensive than hydrocarbon solvents but have the advantage that they are substantially inert under the reaction conditions. Suitable chlorofluorohydrocarbon solvents include "arcton" solvents having an appropriate boiling point. Suitable perfluorohydrocarbon solvents include perfluoroalkanes, perfluoro hydrogenated aromatic compounds such as perfluorodecalin and polymeric or non-polymeric perfluoroalkyl ethers such as perfluoroethyl ethers.

The stoichiometric proportion of silver difluoride is 10 moles of silver difluoride per mole of aryl- or heteroaryl disulphide starting material. It is preferred however to use an excess of silver difluoride, for example at least 12 moles of silver difluoride per mole of aryl- or heteroaryl disulphide. There is no real upper limit to the excess of silver difluoride which may be used if desired, but the use of more than 20 moles of silver difluoride per mole of aryl- or heteroaryl disulphide is unlikely to provide any advantage and may increase the probability of solvent fluorination or of attack on the reaction vessel. We have found that a larger excess of silver difluoride than that described by Sheppard in his paper provides unexpectedly superior yields. A proportion of from 14 moles to 18 moles of silver difluoride per mole of aryl- or heteroaryl disulphide is especially preferred.

The reaction suitably takes place in fluorine-resistant reactor having good heat transfer characteristics. Suitable precautions should be taken to ensure that the reaction takes place under anhydrous conditions and the reaction suitably takes place under a dry, inert atmosphere. The silver difluoride is largely insoluble in the reaction solvent and the reaction mixture is suitably stirred or agitated to ensure effective reaction contact. Silver difluoride consumed during the reaction is converted to silver fluoride which is also insoluble under the reaction conditions.

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Silver fluoride and any unreacted silver difluoride remaining after the reaction is complete are thus readily recovered by filtration, optionally with washing using a suitable solvent. Silver difluoride is readily re-formed by the treatment of silver fluoride with a fluorinating agent such as gaseous fluorine. Thus whilst the excess silver difluoride used in the process of the present invention represents an expensive capital outlay, the silver may be used effectively as a carrier for the fluorine used in the formation of the sulphurpentafluoride moiety and may be re-cycled repeatedly without serious loss.

Thus according to a further aspect of the present invention there is provided a process for the preparation of arylsulphurpentafluorides or heteroarylsulphurpentafluorides which comprises

- a) reacting an aryldisulphide or heteroaryldisulphide with silver difluoride under anhydrous conditions at a temperature of at least 100°C and in the presence of a non-aqueous solvent whose boiling point is at or above the reaction temperature, said solvent being substantially stable under the reaction conditions;
- b) recovering silver fluoride and any unreacted silverdifluoride remaining at completion of reaction stage (a);
- c) treating the silver fluoride and unreacted silverdifluoride recovered in stage (b) with a fluorinating agent to re-convert it to silver difluoride; and
- d) re-cycling the silverdifluoride formed in stage (c) to reaction stage (a).

The reaction may take place either continuously or in a semi-continuous manner whereby the silverfluoride/silverdifluoride recovered from a batch reaction stage (a) is re-converted to silverdifluoride (stage c) and re-cycled to a new batch reaction stage (a).

The reaction time is generally in the range of 6 to 12 hours. The course of the reaction can conveniently be monitored by analysis to detect the presence of the intermediate aryl- or heteroarylsulphurtrifluoride, the reaction being deemed to be complete when no further aryl- or heteroarylsulphurtrifluoride is detected.

The product is suitably recovered following the removal by filtration of silverfluoride and any unreacted silverdifluoride from the reaction mass. It is not essential that the product is completely soluble in the

reaction mixture, and in this case some product may be removed as a solid with the silverfluoride/silverdifluoride. Preferably the silverfluoride/silverdifluoride is washed with either the same solvent used in the reaction or a different solvent and the filtrates are combined. The product may be recovered from the combined filtrates by conventional means such as fractional distillation.

In an alternative to a conventional work-up of the product, the product may be recovered by the use of a second, lower-boiling solvent in which the product is preferentially soluble and which is immiscible with the reaction solvent. The filtered silverfluoride/silverdifluoride is suitably washed with the lower-boiling solvent to recover any product contained therein and the lower-boiling solvent is thereafter agitated with the reaction solvent in a solvent-extraction process whereby the product is extracted into the lower-boiling solvent. The product may be readily recovered from the lower-boiling solvent by conventional means, whilst the reaction solvent may be re-cycled in a continuous reaction or to a subsequent batch reaction stage in a semi-continuous reaction. Suitable reaction solvent and immiscible, lower-boiling solvent combinations will occur to those skilled in the art. This aspect of the invention is illustrated herein by the use of perfluorodecalin or perfluoroethylether as reaction solvent and methylene chloride as a lower-boiling solvent which is immiscible with the reaction solvent and in which the product is preferentially soluble.

The process of the present invention may be applied for example to the preparation of benzenesulphurpentafluoride compounds and pyridinesulphurpentafluoride compounds. Substituents may be present in the aromatic or heteroaromatic ring as illustrated herein. Those skilled in the art will appreciate that not all substituted aryl- or heteroarylsulphurpentafluoride compounds may be prepared directly by the process of the present invention since some such substituents may be susceptible of attack by the fluorinating agent during the reaction or may activate the aryl or heteroaryl ring to attack by the fluorinating agent. Thus it is preferred for example that a ring de-activating substituent such as nitro, trifluoromethyl, pentafluoroethyl, or (di)-halogen be present in a benzene ring to minimise ring fluorination. Substituents such as hydroxy, ester, nitrile and carboxylic acid may be expected to be subject

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to attack by the fluorinating agent and should generally not be present in compounds prepared using the process of the present invention. Those skilled in the art should be able to select those substituted arylsulphurpentafluoride compounds and heteroarylsulphurpentafluoride compounds which are suitable for manufacture by the process of the present invention, but in the case of any doubt routine experiment may be used to determine whether undesirable attack by the fluorinating agent takes place, either on a substituent itself or on the aromatic or heteroaromatic ring.

As specific examples of compounds suitable for manufacture by the process of the present invention, there may be mentioned 4-nitrobenzenesulphurpentafluoride, 3-nitrobenzenesulphurpentafluoride, 2-nitrobenzenesulphurpentafluoride, pyridinesulphurpentafluoride, 2,3-dichloropyridine-5-sulphurpentafluoride.

It will be appreciated that compounds prepared by the present invention may be converted to other compounds which would not themselves be suitable for preparation directly using the process of the present invention. Thus for example nitrobenzenesulphurpentafluoride compounds may be readily converted into aminobenzenesulphurpentafluoride compounds which may in turn be converted to other derivatives as illustrated for example in International Application No GB92/01636 and in other co-pending applications. Numerous other such conversion reactions will occur to those skilled in the art.

The aryl- and heteroaryldisulphide starting materials are known compounds which may be prepared using well known techniques. If desired the disulphide compound may be prepared in situ for example using the corresponding thiol. The corresponding thiol is in many instances a liquid or is readily soluble in typical reaction solvents. This provides advantages should it be desired to feed the thiol to the reaction mixture, for example to minimise the effects of any reaction exotherm.

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

This Example illustrates the preparation of 4-nitrobenzenesulphurpentafluoride.

Octane (450ml) was charged to a copper reaction vessel (1500 ml capacity) fitted with a PTFE closure machined to accept a copper condenser

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and a copper thermocouple pocket, and provided with entry points for charging of solids and liquids and with a mechanical agitator having a rotary seal. 4-Nitrophenyldisulphide (50g) was charged to the reaction vessel and agitation was commenced.

Silver difluoride (400g) was added in one portion to the stirred mixture at ambient temperature from a solid addition funnel designed to maintain an inert atmosphere over the contents during the charging procedure. Last traces of silver difluoride were rinsed into the reactor with (50 mls) of octane. The temperature of the reactor and contents was raised over 2 hours to 122 - 124°C and held at this temperature for 6.5 hours.

The reaction mass was sampled and analysed by HPLC eluted with a methylene chloride/acetonitrile mixture (2:1 v/v), using UV detection at 254nm. Reaction was deemed to be complete when all of the intermediate benzenesulphurtrifluoride had been converted to the desired pentafluoride.

The reaction mass was allowed to cool to ambient temperature and the reaction vessel was then opened and the contents filtered to remove silver fluoride and any unreacted silverdifluoride. The silver fluoride was washed with methylene chloride and the washings were combined with the filtrate, then evaporated under reduced pressure to remove the volatile wash solvent leaving a solution of the product in octane.

The solution of the product was then charged to the top of a dry packed silica column (100mm dia. X 65mm) and allowed to elute leaving the product retained at the top of the column. The column was then eluted with n hexane to remove the last traces of octane and finally the product was eluted with chloroform. The chloroform eluents were evaporated to give 74 grams of product whose purity was estimated as 99% by HPLC whilst GC analysis indicated 16% octane/hydrocarbon content. The yield was thus 78% (based on disulphide charged and GC analysis of purity).

EXAMPLE 2

This Example illustrates the use of an alternative solvent for the preparation of 4-nitrobenzenesulphurpentafluoride.

The general procedure of Example 1 was repeated using the same weights of all reactants and the same volume of nonane in place of octane. The temperature of the reactor and contents was raised over 2 hours to 125 - 130°C and held at this temperature for 3.5 hours.

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The product was isolated as in Example 1 to give 58 grams of product whose purity was estimated as 99% by HPLC whilst GC analysis detected no solvent volatiles. The yield was thus 72% (based on disulphide charged and GC analysis of purity).

EXAMPLE 3

This Example illustrates the preparation of 4-nitrobenzenesulphur-pentafluoride using an alternative solvent.

4-Nitrophenyldisulphide (1.54g) was reacted with silver difluoride (12g) using the general method of Example 1 except that a smaller reactor (220ml capacity) was used. The solvent was a perfluoroethylether solvent sold under the tradename "Galden HT135" and having a boiling point of 135°C. 20ml of solvent was used in the initial charge to the reactor and an additional 15mls were used to rinse the silverdifluoride into the reactor. The temperature of the reactor and contents was raised to 125-130°C over 1.5 hours and held at that temperature for 7 hours.

The reaction mass was allowed to cool to ambient temperature and the reaction vessel was opened and the contents filtered to remove silver fluoride/silverdifluoride. The filtered solids were washed with methylene chloride (4x20ml) and the filtrate was extracted with fresh methylene chloride (2x20ml). The perfluoroethylether solvent was available for further reaction. The combined methylene chloride extractions/washings were evaporated under reduced pressure to remove the volatile solvent, yielding 2.4g of product whose purity was estimated as 99% by HPLC whilst GC indicated 11% volatile solvent, 9% of other volatiles and 65% product. The yield (based on disulphide charged and GC analysis of purity) was thus 64%.

EXAMPLE 4

This Example illustrates the preparation of 4-nitrobenzenesulphur-pentafluoride using an alternative solvent.

4-Nitrophenyldisulphide (1.54g) was reacted with silver difluoride (12g) using the general method of Example 1 except that a smaller reactor (220ml capacity) was used. The solvent was hexafluoro-1,1,3,4-tetrachlorobutane. 18ml of solvent was used in the initial charge to the reactor and an additional 12mls were used to rinse the silverdifluoride into the reactor. The temperature of the reactor and contents was raised to 125-129°C over 1.5 hours and held at that temperature for 7 hours.

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The reaction mass was allowed to cool to ambient temperature and the reaction vessel was opened and the contents filtered to remove silver fluoride/silverdifluoride. The solids were washed with methylene chloride (5x20ml) and the resultant wash was evaporated under reduced pressure and the recovered product was re-dissolved in the reaction filtrate. This solution was applied to the top of a dry-packed silica column (50mm diameter x85mm) and the fluorocarbon removed by elution with hexane. After sucking dry the silica was extracted by slurrying twice in chloroform, which on evaporation yielded the desired product (2.18g). The purity of the product was estimated as 91% by HPLC with adjacent peak, 9% (sulphonyl fluoride species derived from arylsulphurtrifluoride impurity prior to silica column treatment). GC indicated 84% purity with low volatile solvent content. The yield (based on disulphide charged and GC analysis of purity) was thus 75%.

EXAMPLE 5

The procedure of Example 3 was repeated using the same weights of reactants and the same volume of perfluorodecalin in place of the perfluoroethyl ether. The temperature of the reactor and contents was raised to 127-130°C over 1.5 hours and held at that temperature for 10 hours.

The reaction mass was allowed to cool to ambient temperature and the reaction vessel was then opened and the contents filtered to remove silver fluoride/silverdifluoride. The solids were washed with methylene chloride and the washings were used to extract the filtrate, which was then further extracted with fresh methylene chloride. The remaining perfluorodecalin was available for re-cycling to a further reaction. The combined extractions were evaporated under reduced pressure to remove the volatile solvent, yielding 2.14 grams of product.

The purity of the product was estimated as 99% by HPLC whilst GC indicated 88% purity with 4% volatile solvent content. The yield (based on disulphide charged and GC analysis of purity) was thus 77%.

EXAMPLE 6

This Example illustrates the preparation of 3-nitrobenzenesulphur-pentafluoride.

The procedure of Example 1 was repeated using the same weights of reactants except that 3-nitrophenyldisulphide was used in place of

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4-nitrophenyldisulphide and the weight of silverdifluoride was increased to 410g. Equal volumes of nonane were used in place of octane.

The temperature of the reactor and contents temperature was raised to 60° and held at this temperature for 35 minutes. The temperature was then raised further over 75 minutes to 125-130°. The temperature was held in this range for 10 hours at which time less than 7% of the intermediate aryl sulphur trifluoride remained.

The product was recovered as in Example 1 to give 39 grams of product. The purity of the product was estimated as 99% by HPLC, whilst GC detected nonane/hydrocarbons at low level.

EXAMPLE 7

This Example illustrates the preparation of 2-pyridylsulphur-pentafluoride.

Nonane (40ml) was charged into the reaction vessel described in Example 3. Agitation was commenced and silver difluoride (18.0g) was added at ambient temperature. Last traces of silver difluoride were rinsed into the reactor with 20 mls of nonane. 2-Pyridyldisulphide was charged to the agitated slurry of silver difluoride at ambient temperature and reactor and contents were slowly heated to 120°C and held at this temperature for 5 hours. After this time a sample was withdrawn and analysed by ¹⁹F NMR which indicated that almost all the sulphurtrifluoride intermediate had been converted to the desired product.

The reaction mass was allowed to cool to ambient and the reaction vessel was then opened and the contents decanted. The remaining silver fluoride/silverdifluoride was washed with 3X 20ml of methylene chloride and retained. The nonane solution of the product was then charged to the top of a dry packed silica column (5 cm dia. X11 cm) and allowed to elute leaving the product retained at the top of the column. The column was then eluted with n-hexane (150ml) to remove the last traces of the reaction solvent and finally the product was eluted with methylene chloride. All the methylene chloride solutions were combined and distilled at atmospheric pressure to give 7mls of crude product which was further purified to give 2.7g of a straw coloured liquid whose purity was estimated by GC as 70%. The yield (based on disulphide charged and GC determination of purity) was 68%.

The structure of the product was confirmed by NMR and ¹⁹F NMR:-

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^{19}F NMR 51.3-51.8(4F d) 77.1-79.4(1F pent)

^1H NMR $\delta(\text{CDCl}_3)$ 7.37-7.43(1H,m) 7.67-7.7(1H,d) 7.84-7.89(1H,m)
8.51-8.54(1H,m).

COMPARISON

4-Nitrobenzenesulphurpentafluoride was prepared using the method described in Sheppard W.A. J.A Chem Soc 84 3064, (1962).

1,1,2-Trichlorotrifluoroethane (18ml) was charged to the copper reaction vessel described in Example 3. 4-nitrophenyldisulphide (6g) was charged and agitation commenced. Silver difluoride (35.1g) was added in one portion to the stirred solvent/dispersant at ambient temperature from a solid addition funnel designed to maintain an inert atmosphere over the contents during the charging procedure. Last traces of silver difluoride were rinsed into the reactor with (8mls) of the solvent /dispersant.

The reactor and contents were heated to 50°C and held at this temperature for one hour. The 1,1,2-trichlorotrifluoroethane was distilled out and the reactor was then heated to 125-131°C and held at this temperature for 2 hours. Heating was stopped and the reactor and contents were allowed to cool to 35°. Methylene chloride (25ml) was then charged and stirred 5 minutes; the reactor was opened and the silver fluoride filtered off. This was washed with more methylene chloride (3x25ml), then chloroform (2x25ml).

The final workup and isolation was changed from the original literature method in order to permit a fair comparison of isolated yields. Thus the methylene chloride and chloroform filtrates/washes were combined and evaporated under reduced pressure to give the a product (8.28g) which was dissolved in nonane. The nonane solution of the product was charged to the top of a dry packed silica column (43mm dia.x 45mm) and allowed to elute leaving the product retained at the top of the column. The column was then eluted with n-hexane to remove the last traces of nonane and finally the product was eluted with chloroform.

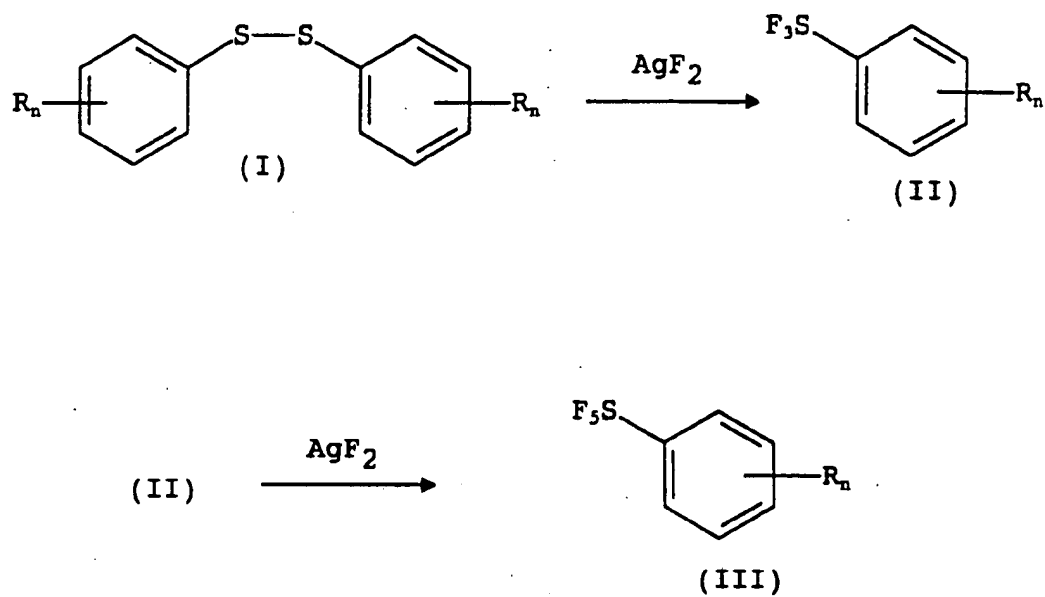
The chloroform eluent was evaporated to give 2.4g of product. The purity of the product was estimated as 99% by HPLC, whilst GC showed no detectable solvents. The yield was thus 25% (based on disulphide charged and GC estimate of purity).

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CHEMICAL FORMULAE

(IN DESCRIPTION)

Scheme 1



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CLAIMS

1. A process for the preparation of arylsulphurpentafluorides and heteroarylsulphurpentafluorides which comprises reacting an aryldisulphide or heteroaryldisulphide with silver difluoride under anhydrous conditions at a temperature of at least 100°C and in the presence of a non-aqueous solvent whose boiling point is at or above the reaction temperature, said solvent being substantially stable under the reaction conditions.
2. A process according to claim 1 wherein the reaction temperature is from 110°C to 150°C.
3. A process according to claim 2 wherein the reaction temperature is from 120°C to 140°C.
4. A process according to any of the preceding claims wherein the solvent is a hydrocarbon, a chlorofluorohydrocarbon or a perfluorohydrocarbon having a boiling point at a temperature at or above the reaction temperature.
5. A process according to any of the preceding claims wherein the solvent is octane, nonane, perfluoroethylether, hexafluoro-1,2,3,4-tetrachlorobutane or perfluorodecalin.
6. A process according to any of the preceding claims wherein there is used at least 12 moles of silver difluoride per mole of aryl- or heteroaryldisulphide.
7. A process according to claim 6 wherein there is used from 14 to 18 moles of silver difluoride per mole of aryl- or heteroaryldisulphide.
8. A process according to any of the preceding claims wherein the aryl- or heteroaryldisulphide is 4-nitrophenyldisulphide, 3-nitrophenyldisulphide, 2-nitrophenyldisulphide or 2-pyridyldisulphide and the respective products are

4-nitrobenzenesulphurpentafluoride,
3-nitrobenzenesulphurpentafluoride, 2-nitrobenzenesulphurpentafluoride,
pyridinesulphurpentafluoride,
2,3-dichlorpyrdine-5-sulphurpentafluoride.

9. A process for the preparation of arylsulphurpentafluorides or heteroarylsulphurpentafluorides which comprises
 - a) reacting an aryl disulphide or heteroaryl disulphide with silver difluoride under anhydrous conditions at a temperature of at least 100°C and in the presence of a non-aqueous solvent whose boiling point is at or above the reaction temperature, said solvent being substantially stable under the reaction conditions;
 - b) recovering silver fluoride and any unreacted silver difluoride remaining at completion of reaction stage (a);
 - c) treating the silver fluoride and unreacted silver difluoride recovered in stage (b) with a fluorinating agent to re-convert it to silver difluoride; and
 - d) re-cycling the silver difluoride formed in stage (c) to reaction stage (a).

INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/GB 94/00740

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 C07C381/00 C07D213/71

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 84, no. 16, 28 August 1962 Washington, DC, US, pages 3064 - 3072 W.A. SHEPPARD: 'Arylsulphur pentafluorides' cited in the application see the whole document ---	1-9
X	CHEMICAL ABSTRACTS, vol. 117, no. 8, 24 August 1992, Columbus, Ohio, US; abstract no. 70558w, page 16 ; & U.S. PATENT APPLICATION US 755,207 (A.K. ST. CLAIR, ET AL.) 1 March 1992	1-4
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☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

6 June 1994

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